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MECHANISM OF CATALYSIS WITH THE THERMAL DECOMPOSITION AND BURNING OF AMMONIUM PERCHLORATE

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Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е в	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yë or ë.
The use of diacritical marks is preferred, but such marks
may be omitted when expediency dictates.

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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

———

Russian	English
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	⍺	Nu	N	ν
Beta	B	β		Xi	Ξ	ξ
Gamma	Γ	γ		Omicron	O	o
Delta	Δ	δ		Pi	Π	π
Epsilon	E	ε	ϵ	Rho	P	ρ	ϱ
Zeta	Z	ζ		Sigma	Σ	σ	ς
Eta	H	η		Tau	T	τ
Theta	Θ	θ	ϑ	Upsilon	Υ	υ
Iota	I	ι		Phi	Φ	φ	ϕ
Kappa	K	𝓃	κ	ϰ	Chi	X	χ
Lambda	Λ	λ		Psi	Ψ	ψ
Mu	M	μ		Omega	Ω	ω

MECHANISM OF CATALYSIS WITH THE THERMAL DECOMPOSITION AND BURNING OF AMMONIUM PERCHLORATE

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Novosibirsk

Although the role of the reactions of the decomposition of
perchloric acid with the decomposition and burning of ammonium
perchlorate (PCA) and in the catalysis of these processes was
already repeatedly stressed [1-4], quantitatively the connection
between them was not checked mainly due to the absence of reliable
kinetic data. At the same time such data are basis for the
construction of models of burning of the PCA and fuels on its base,
and also a model of catalysis with burning. Given in this work are
results of kinetic studies of the decomposition (including catalytic)
of the PCA and mixture $HClO_4 + NH_3$, which are used for finding the
quantitative connection between these processes and for the con-
struction of models of burning of the PCA and catalysis of burning.

A study of the kinetics of the decomposition of mixtures
$HClO_4 + NH_3$ was conducted with 20 mm Hg in a Lossing flow reactor
connected through the diaphragm with the ionic source of a time-of-
flight mass-spectrometer (Fig. 1). The mixture $HClO_4 + NH_3$ was
obtained with the sublimation of the PCA in one of the furnaces at

350°C and by the flow of helium was transferred to the radial clearance heated by the second furnace between two coaxial tubes, on surface of one of which the catalyst was applied by a thin (1 µm) layer. By means of changing the retention time it was shown that the decomposition reaction of $HClO_4$ on the catalyst Fe_2O_3 is of the first order. Figure 2 shows the dependence of the concentrations of different components on the temperature, obtained as a result of the processing of the mass spectra, at the fixed retention time $(3.6 \cdot 10^{-3}$ s). The reaction rate of the decomposition of $HClO_4$ at 376–430°C is equal to

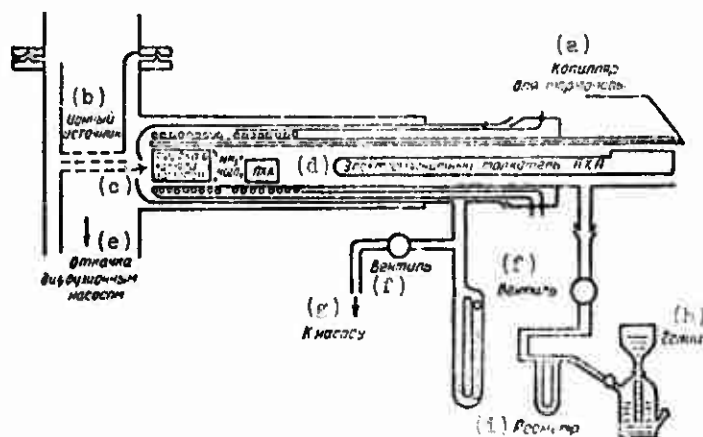$$k_{y\text{д}} = 6.7 \cdot 10^{14} \exp(-28500/RT) \text{ cm}^3/\text{s per gram of catalyst.} \quad (1)$$

Figure 1

Figure 1. Diagram of the reactor in combination with the mass-spectrometer for a study of the catalytic decomposition of the mixture $HClO_4 + NH_3$.
Key: (a) capillary for a thermocouple; (b) ionic source; (c) tube with catalyst; (d) electromagnetic push rod of PCA; (e) pumping by diffusion air pump; (f) valve; (g) to the pump; (h) helium; (i) rheometer.
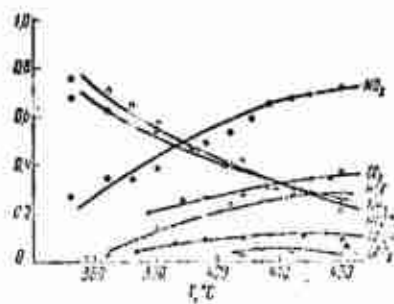
Figure 2. Dependence of the relative (to $HClO_4$) concentrations of components on temperature for the system $HClO_4 + NH_3 + Fe_2O_3$.

After a stay in the combustion zone of PCA, the specific surface area and catalyst activity of Fe_2O_3 are decreased by 3–4 times. The catalyst MnO_2 is considerably [illegible], and CuO is less active

than Fe_2O_3. The CuO, Cr_2O_3 and $CuCr_2O_4$ enter into a reaction with $HClO_4$ with the formation of volatile compounds, which by the flow of helium are carried away from the reaction zone.

With the use of the derivative-graphic method in air with a linear increase in the temperature (~8 degrees/min) in a quartz crucible, which consists of two coaxial tubes between which there was placed a suspension (40 mg) of powder of PCA with particle sizes on the order of 100 µm, the kinetics of the high-temperature decomposition of PCA, pure and with a catalyst, is studied. Results of the experiments are represented on Fig. 3. The reaction rate of the decomposition of PCA+2.5% Fe_2O_3 in the range of 320-370°C is equal to

$$\frac{d\alpha}{dt} \cdot \frac{1}{(1-\alpha)} = 3,3 \cdot 10^{16} \exp(-52100/RT) \; 1/s, \tag{2}$$

where α is the degree of transformation of the PCA.
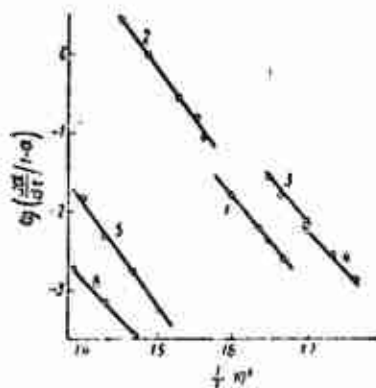

Figure 3. Temperature dependences of the reaction rate of the decomposition of PCA: 1 - PCA+2.5% Fe_2O_3; 2 - calculation according to (3); 3 - PCA+2.5% CuO; 4 - PCA+2.5% MnO_2; 5 - pure PCA; 6 - calculation under the assumption of a gas-phase reaction.

The calculation of the decay rate of the PCA+2 5% Fe_2O_3 with the use of (1) and formulas given in work [2], derived on the assumption that with thermal decay there manages to be established the equilibrium pressure of the $HClO_4$ above the PCA, gives

$$\left(\frac{d\alpha}{dt}\right)_{\alpha \to 0} = 4 \cdot 10^{16} \exp(-57200/RT) \; 1/s. \tag{3}$$

Values of the calculated (3) and measured (2) decay rate of the PCA agree with the accuracy up to the error of the experiment (Fig. 3), which serves as a quantitative confirmation of the hypothesis [2] relative to the mechanism of the catalytic decomposition of the PCA.

the greater effectiveness of the copper oxide in experiments on the thermal decay of the PCA (Fig. 3) than in experiments on the decomposition of $HClO_4$ (in comparison with MnO_2 and Fe_2O_3) is connected with the formation in the process of the reaction of $HClO_4$ with CuO of the catalyst CuCl, considerably more active than CuO, volatile at 400°C, which in the first case does not manage to diffuse from the zone of reaction, and under conditions of the flow it is taken away from this zone.

Proofs of the fact that in our experiments the high-temperature decomposition of pure PCA flows to a greater degree (more than 80%) in the condensed phase and to a lesser degree - in the gaseous phase, are represented in Fig. 3, where curve 5 corresponds to the measured reaction rate of the decomposition of pure PCA ($E \approx 60$ kcal/mole), and curve 6 is the calculated curve with the use of formulas of source [2] on the assumption that the decomposition of $HClO_4$ occurs in the gaseous phase with the Levy constant [5] (in the calculation the design of the crucible was considered). Furthermore, with a change of 5 times of the parameters which determine the reaction rate in the gaseous phase (reaction volume of the crucible, area of the ring cross-section), the rate of decomposition was changed by 20-30%.

The findings make it possible to construct a model of the burning of the PCA and model of the catalysis of the burning of monofuels, which, in our opinion, are more valid than those known at present [6]. The first model is based on the three positions checked by us experimentally at 450°C:

1) on the burning surface the equilibrium pressure of $HClO_4 + NH_3$ is established;

2) there occurs a surface exothermal reaction with the constant calculated from experiments on the decomposition of pure PCA (Fig. 3, curve 5);

3) the decomposition reaction of the mixture $HClO_4 + NH_3$ is a first-order reaction for $HClO_4$ and zero for NH_3.

Results of the numerical calculation on a computer of this model give the absolute values close to the experimental data of the rate of combustion and exponent in the law of burning, $\nu \approx 0.9$ (Fig. 4); although they do not explain the upper limit of burning according to pressure.
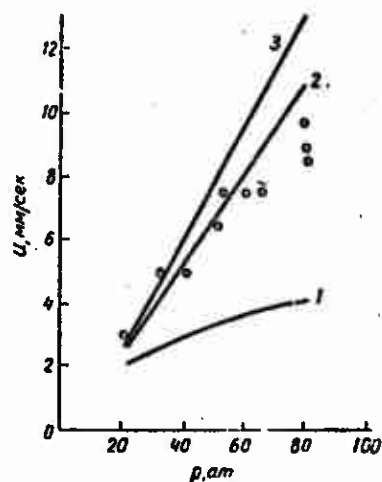

Figure 4. Dependence of the rate of combustion of the PCA on pressure: 1 – calculation without surface reaction; 2 – calculation taking surface reaction into account; 3 – calculation taking into account surface and catalytic reaction (o – experimental data).
Abbreviations: сек = s; ам = at.

Two means of the effect of the catalyst are possible: in the gas and condensed phases. In this case there can be two conditions of the catalysis: diffusion and kinetic.

The effectivenesses measured by us experimentally and calculated from the above-mentioned model on a computer for the subdispersion particles of Fe_2O_3 (kinetic condition with constant (1)) of the action of the catalyst on the rate of combustion prove to be similar in value. The transition from kinetic condition to diffusion, according to the calculations, occurs with a change in the particle size of Fe_2O_3 (d) from 0.1 to 1 μm. Upon the consideration of the reaction which takes place on particles of the catalyst located on the burning surface, the heat flux into the condensed phase with the kinetic condition will increase by $\Delta Z_{\text{к}}$.

$$\Delta Z_{\text{к}} = d_{\text{к}} f \rho_{\text{к}} k_{\text{уд}} \rho_{\text{п}} Q, \qquad (4)$$

where $\rho_{\text{к}}$, $\rho_{\text{п}}$ are densities of the catalyst and reacting gas near the burning surface; f - weight fraction of the catalyst in the condensed phase; Q - thermal effect of the reaction.

As can be seen from (4), $\Delta Z_{\text{к}}$ increases with an increase in $d_{\text{к}}$; however, with large grain sizes, when the reaction passes into the region of diffusion and expression (4) will not be valid, $\Delta Z_{\text{к}}$ decreases with an increase in $d_{\text{к}}$. Hence it follows that on the curve *effectiveness of the catalyst-dispersion* the maximum must exist. The account of two means of the effect of the catalyst eliminates some contradictions of the theory of the "maximally strong catalysis in the gaseous phase" (for example, in the question of the effect of the dispersion of the catalyst). For the experimental check of the theory it would be necessary to have monodisperse particles of the catalyst. However, in a number of cases there appear additional difficulties, for example, the melting also of the agglomeration of the particles on the burning surface, as was revealed by us by microscopic and electron-microscopic examinations of the surface of the extinguished specimens of PCA+2% CuO (here with a decrease in pressure in the bomb from 80 to 1 at the particles become larger).

Calculations on the computer were made by A. V. Tatevosyan, to whom the authors express their gratitude.

BIBLIOGRAPHY

1. A. R. Hall, G. S. Pearson. Oxidation and Com. Rev., Elsevier, 1968, 3.
2. О. П. Коробейничев. Кинетика и катализ, 1968, 5, стр. 1169.
3. F. Solymosi, L. Gera, S. Börcsök. XIII-th International Symposium on Comb. Abstract, p. 154.
4. О. П. Коробейничев, Ю. Я. Карпенко, В. В. Болдырев. Изв. АН СССР, сер. хим., 1970, 7, стр. 1663.
5. J. B. Levy. J. Phys. Chem., 1962, 66, p. 1092.
6. M. Barrere, F. A. Williams. AGARD Comb. and Propuls. Panel, 25-th Meeting, La Jolla, USA, 1965.